

PATENT SPECIFICATION

993,434



NO DRAWINGS

993,434

Date of Application and filing Complete Specification: Feb. 15, 1962.

No. 5782/62.

Application made in Germany (No. B61292 IVd/39c) on Feb. 16, 1961.

Complete Specification Published: May 26, 1965.

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Index at acceptance:—C8 P(11C13A, 11C13B, 11C13C, 11D5, 11K11, 11P4C, 11P8X, 11T2A, 11T2D); C8 R(3T2, 22T2, 33P)

Int. Cl.:—C 08 g

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are HANS CRAUBNER and GERHARD ILLING, Citizens of Germany and residents, respectively, of 230 Kriegsstrasse, Karlsruhe, Germany; and 3a Schlossberg, Neuleiningen/Pfalz, Germany.

COMPLETE SPECIFICATION

Production of Block Graft Polymers from Polyformaldehyde and other Thermoplastics

We, H. RÖMMLER G.M.B.H., a German Company of Gross-Umstadt, Odervald, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

According to a proposal for the nomenclature in the field of macromolecular substances (Makr. Ch. 38 (1960) 1) by graft polymers there are to be understood branched polymers in which the side chains are structurally different from the main chain. According to the same proposal, block polymers are linear polymers into the polymer chain of which segments are built in, which are built up from monomers of a different type and which contain as units a large number of identical monomers. By block graft polymers there are to be understood polymers in which blocks or chains of polymers or polycondensates with monomer units B are grafted onto polymer chains of a different type having monomer units A, and of which the polymer chains

A AAAABBB BBB 30
 B
 B
 B
 B

It has been proposed in the British Patent Specification No. 927,968 to prepare block graft polymers by homogenisation of mixtures of polyolefines and polycondensates containing carbonamide groups in the presence of catalysts, such as organic peroxides, at temperatures between 50° and 350° C. It has also been proposed in British Patent Specification No. 919,098 to prepare block graft polymers by reacting polyolefines in a melt with wholly or partly nitrosated polycondensates containing carbonamide groups and, if desired, additionally with olefinically unsaturated monomers. According to another proposal, described in the French Patent Specification No. 1,307,186 which was not published at the

[Proprietary Mark]

- priority date of the present application, modified olefine polymers are obtained by intensely kneading mixtures of different olefine polymers with an addition of radical-forming substances, such as organic peroxides, at temperatures between 80° and 350°C. 5
- We have now found that block graft polymers with advantageous properties can be prepared by intensely kneading high molecular weight polyformaldehyde with one or more other thermoplastic synthetic resins with the addition of a small amount of one or more free radical forming organic catalysts. 10
- By intensely kneading we mean subjecting the charge to kneading in multishaft extruders and kneaders and also refiners and calenders having a plurality of differential twin rolls, as hereinafter described. Suitable high molecular weight polyformaldehyde may be prepared in conventional manner and advantageously has a melt index between 8 and 40 g/10 min at 190°C. Thermoplastic synthetic resins suitable for the purposes of this invention are for example polycondensates which, at a temperature 15 10°C above their melting point, have a melt index between 0.4 and 50, preferably between 1 and 40, g/10 min., such as preferably linear synthetic polyamides, which can be prepared in the conventional way from lactams, such as caprolactam, oenantholactam, caprylolactam or the lactam of ω -amino-lauric acid, or from dicarboxylic acids, such as adipic, suberic, sebacic or heptadecanedicarboxylic acid, and diamines, such as hexamethylene diamine, octamethylene diamine, decamethylene diamine, dodecamethylene diamine, 1,4-diaminomethylbenzene, 1,4-diaminomethylcyclohexane and 4,4'-diamino-dicyclohexylmethane, or polyamide esters 20 25 30 35 40 45 50 55 60 65
- which can be prepared in the conventional way from dicarboxylic acids, such as adipic acid, succinic acid, maleic acid or sebacic acid, and aminoalcohols, such as ethanolamine, 6-aminohexanol and 6-amino-2-ethylhexanol, or such dicarboxylic acids and mixtures of diols, such as butanediol-1,4, hexanediol-1,6, octanediol-1,8 and decanediol-1,10, and diamines, such as hexamethylene diamine, octamethylene diamine and decamethylene diamine, and also polyureas, polythioureas, polurethanes and polyesters, as for example polyethylene glycol terephthalate, all of which may be prepared in the conventional way. Other suitable thermoplastic synthetic resins are high molecular weight polymers with melt indexes at 230°C between 0.3 and 50 obtainable in conventional manner from olefinically unsaturated monomers, as for example from mono- and diolefines with two to six carbon atoms, such as ethylene, propylene, isobutylene, butene-1, isoprene, butadiene, 2 - chlorobutadiene, 2,3 - dimethylbutadiene, vinyl halides, such as vinyl and vinylidene chloride and fluoride, tetrafluoroethylene, trifluorochloroethylene, derivatives of α,β -un- 70 75 80 85 90 95 100 105 110 115 120 125
- saturated aliphatic mono- and dicarboxylic acids, such as acrylonitrile, methacrylonitrile, acrylic acid and methacrylic acid and their methyl, ethyl, propyl, isobutyl, 2-ethyl, decyl and cyclohexyl esters, acrylamide, methacrylamide, N-methacrylamide, N,N-methylene-dimethacrylamide, vinyl ethers, such as methyl, isopropyl, butyl, dodecyl, cetyl and stearyl vinyl ethers, vinyl esters, such as vinyl acetate, vinyl propionate and vinyl stearate, heterocyclic compounds substituted by vinyl groups, such as N-vinylpyrrolidone, N-vinyl-carbazole and N-vinylimidazole, vinyl-aromatic compounds which contain one benzene nucleus, such as styrene, α -methylstyrene, α -chlorostyrene, vinyltoluenes, divinylbenzene and *p*-isopropylvinylbenzene, olefinically unsaturated aliphatic dicarboxylic acids, such as maleic acid, dichloromaleic acid, fumaric acid, itaconic acid, mesaconic acid and citraconic acid, and their amides or esters with aliphatic alcohols, such as methanol and ethanol, and also vinylsulphonic acids and their esters. Other suitable thermoplastic synthetic resins are for example polyvinyl alcohols, polystyrene chlorinated in the conventional way and polyvinyl chloride, as well as polyethylene sulphochlorinated in conventional way or crosslinked for example by irradiation. 130
- Catalysts which are suitable for the process according to this invention are especially those which decompose into radicals at temperatures between 50° and 260°C, which have an average life of about ten seconds to twenty minutes, as for example especially organic peroxides, such as cumene hydroperoxide, dicumyl peroxide, tert.-butylhydroperoxide, di - tert. - butyl peroxide, 2,5 - ditert. - butylperoxy - 2,5 - dimethylhexane, dibenzoyl peroxide, lauroyl peroxide, tert.-butyl perbenzoate, and also azo-bis-nitriles, such as azo-bis-isobutyronitrile and azo disulphonates. The catalysts may also be used in the form of their solutions in suitable solvents, as for example benzene, toluene, xylenes, dioxane, cyclohexane, methanol, dimethylformamide, carbon tetrachloride or water. 100
- In accordance with this invention the components of the said types are intensely kneaded at temperatures between 50° and 260°C, preferably between 100° and 210°C. Multishaft extruders and kneaders and also refiners and calenders having a plurality of differential twin rolls are especially suitable for kneading. Such machines are the better suited to the process according to this invention the greater the shear stresses are which are produced therein by the boundary surfaces moving relatively to each other. By boundary surfaces moving relatively to each other we mean for example the wall of the extruder chamber and the surface of the screw in screw extruders or especially the cylinder wall and the surface of the blades in multishaft kneaders. The shear stresses occurring in the machines advantageously lie 110

- between 100 and 1.5×10^3 kg/sq.cm. or more and the velocity gradients occurring therein between about 10 and 2000 seconds⁻¹ or more. 45
- 5 The relative proportions of high molecular weight polyformaldehyde and the other thermoplastic synthetic resins may be varied within wide limits. The proportion of polyformaldehyde is advantageously between 1 and 10 99%, preferably between 5 and 95%, by weight. 50
- In the process according to this invention, the components may first be premixed in conventional mixers, as for example propeller mixers, and supplied to the machines in which their reaction is to be carried out by the use of conventional metering devices, such as vibrating channels, belt conveyers, proportioning screws and belt-type weigh feeders. 55
- 15 It is also possible however to supply the components to the machines of the said type separately. The process according to this invention may be carried out batchwise and also, with advantage, continuously. Additives, 20 as for example pigments, fillers, and dyes and stabilisers which do not react with the catalysts used under the conditions of kneading, 25 may be added. 60
- By the process according to this invention, 30 block graft polymers are obtained which exhibit a homogeneous structure and the physical and chemical properties of which lie between those of polyformaldehyde and the thermoplastic synthetic resins used. In 35 general they have thermoplastic properties and may be processed into shaped articles, such as threads, filaments, fibres, bristles and sheets by the conventional methods, for example by injection moulding, extrusion, melt 40 spinning or deep drawing and also by machining, and may be used for the production of 65
- household articles, machine parts, such as gears and casings. The block graft polymers may also be mixed homogeneously in any proportions with polyformaldehyde and thermoplastic synthetic resins of the above-mentioned types. 70
- The invention is illustrated by, but not limited to, the following Examples. The parts specified are by weight. 75
- EXAMPLE 1.** 80
- 10 parts of polyformaldehyde prepared in conventional manner is intensely mixed with 90 parts of high-pressure polyethylene in a propeller mixer and 0.5 part of tertiarybutyl peroxide is sprayed uniformly onto the mixture at 20°C with intense stirring. The mixture is then introduced continuously into a commercially available two-shaft disc kneader and kneaded intensely therein for 60 to 90 seconds at 190° to 210° C.
- A homogeneous thermoplastic block graft polymer is obtained which absorbs 0.17% by weight of water upon lying for an hour in boiling water. The polyformaldehyde used as initial material absorbs 1.8% by weight of water under the same conditions.
- The physical properties of the block graft polymer (a) are compared in the following Table 1 with the properties of the polyformaldehyde (b) and high-pressure polyethylene (c) used as initial materials and a mixture of 10 parts of polyformaldehyde and 90 parts of high pressure polyethylene prepared without adding a catalyst but under otherwise identical conditions (d). The columns in the Table are: A—the property measured; B—the standard by which the measurement is carried out; C—the measured values for the four materials; and D—the units in which the measurement is expressed.

TABLE 1

A	B	C			D	
		a	b	c	d	
Melt index at 190° C.	ASTMD 1238—T	0.16	8.7	1.4	0.82	g/10 min.
Density	DIN 53479	1.01	1.425	0.918m	1.0	g/cc
Softening range		146—158	175—185	103—105	I. 105—110 II. 170—180	°C.
Dielectric constant at 10 ⁴ cycles/sec.	DIN 53483	2.5	3.7	2.3	2.5	
Dissipation factor tan δ at 10 ⁴ cycles/sec.	DIN 53483	0.001	0.004	0.001	0.001	

ΔΔ — two softening ranges.

- The block graft polymer is suitable for the production of injection mouldings, hollow articles and sheets and may be homogeneously mixed with polyethylene. 30
- 5 A mixture of 10 parts of the block graft polymer and 90 parts of high-pressure polyethylene having the properties given in Table 1 is intensely kneaded at 150° to 190°C for about two minutes in a commercially available 35
- 10 rubber kneader and then rolled out to sheets in a rolling mill. Elastic sheets are obtained having a greater dimensional stability than those prepared solely from high-pressure polyethylene having the stated properties. The 40
- 15 sheets may be processed into shaped articles by the deep drawing method or used for electrical insulation. The mixture has the density 0.935 g/cc and the softening range 116° to 117°C. 45
- 20 If 1 part of the block graft polymer is kneaded with 99 parts of high-pressure polyethylene having the stated properties, a modified polyethylene is obtained having the density 0.896 g/cc and the softening range 112° to 115°C; as compared with the unmodified 50

polyethylene, this gives better results when dyeing with acid, vat and dispersion dyes.

EXAMPLE 2.

Various amounts of polyformaldehyde (PF) and polypropylene (PP), both prepared in the conventional way, are intensely kneaded for about 40 to 90 seconds at 190° to 205°C in a twin-shaft disc type kneader with the addition of cumene hydroperoxide (CHP), dicumyl peroxide (DCP) or tertiarybutyl peroxide (DTBP) as catalyst. Block graft polymers are obtained the physical properties of which are compared in the the following Table 2 with the properties of the polyformaldehyde or polypropylene used as initial materials and mixtures of the same composition prepared from the same polymeric initial materials without adding a catalyst but under otherwise the same conditions.

In Table 2, column D gives the density in g/cc in accordance with DIN 53479; column S gives the softening range in °C and column M gives the melt index according to ASTMD 1238—T measured in g/10 min. In the cases marked Δ there are two softening ranges. 50

TABLE 2

Composition of mixture in parts

PF	PP	DTPB	CHP	DCP	D	S	M
100	—	—	—	—	1.423	183 — 185	15.6 at 190° C.
—	100	—	—	—	0.896	128 — 133	0.38 at 190° C.
90	10	1.0	—	—	1.38	185 — 188	32.0 at 190° C.
70	30	1.0	—	—	1.37	180 — 185	2.85 at 175° C.
50	50	1.0	—	—	1.27	178 — 182	0.34 at 175° C.
18	82	0.2	—	—	1.02	168 — 173	1.1 at 198° C.
10	90	0.8	—	—	1.11	162 — 170	12.9 at 190° C.
5	95	0.8	—	—	1.11	158 — 161	11.8 at 175° C.
5	95	—	1.0	—	1.10	164 — 169	10.2 at 175° C.
5	95	—	—	1.0	1.09	148 — 158	60.8 at 175° C.
					I.	160 — 164	
90	10	—	—	—	1.37	Δ II. 180 — 184	11.4 at 190° C
50	50	—	—	—	1.15	Δ I. 160 — 166	4.6 at 190° C.
5	95	—	—	—	0.92	ΔΔ I. 162 — 166	0.8 at 190° C.
					II. 180 — 182		

Homogeneous clear sheets may be prepared from the block graft polymers prepared according to this invention (even when they contain 90% PF) by blow moulding. These sheets cannot however be prepared from mixtures of polyformaldehyde and polypropylene prepared without adding a catalyst.

The block graft polymers prepared according to this invention may be homogeneously mixed with the polyformaldehyde used as initial product and also with polyolefins, such as polyethylene and polypropylene.

(a) A coarse mixture of 10 parts of a block graft polymer derived from 10 parts of polyformaldehyde and 90 parts of polypropylene are mixed with 90 parts of high-pressure polyethylene having the properties specified in Table 1, and this mixture is intensely kneaded for about one to two minutes at 170° to 200° C and then granulated in the conventional way. A homogeneous modified polyethylene is obtained which has the density 0.960 g/cc and the softening range 114° to 126° C and which may be used for the production of mouldings by the injection moulding method. Mouldings are thus obtained which, as compared with those from unmodified high-pressure polyethylene, exhibit an improved thermal stability under load and give better results in dyeing with acid, vat and dispersion dyes.

(b) By using 90 parts of polypropylene having the properties set out in Table 2 instead of the high-pressure polyethylene used under

(a), a modified polypropylene is obtained under otherwise the same conditions which has the density 0.948 g/cc, the softening range 135° to 138° C and which lends itself admirably to spinning into threads, filaments and fibres. Compared with unmodified polypropylene, the modified polypropylene has improved dyeability.

EXAMPLE 3.

Various amounts of polyformaldehyde (PF) having the properties given in Table 2 and prepared in the conventional way are intensely kneaded for 60 to 90 seconds in a twin-shaft disc type kneader at about 190° to 205° C with polycaprylolactam (PC) prepared in the usual way and having the softening range 198° to 203° C and the melt index 0.08 g/10 min. at 190° C, with the addition of ditertiary-butyl peroxide (DTBP), cumene hydroperoxide (CHP) or dicumyl peroxide (DCP) as catalyst. Block graft polymers are obtained the properties of which are compared in the following Table 3 with the properties of mixtures of the same composition prepared from the same polymeric initial materials without the addition of catalyst and under otherwise identical conditions. Column D gives the density in g/cc according to DIN 53479; column S gives the softening range in °C; and column M gives the melt index according to ASTMD 1238—T in g/10 min.

TABLE 3
Composition of mixture in parts

PF	PC	DTPB	CHP	DCP	D	S	M
2	98	1	—	—	1.21	196 — 200	0.82 at 218° C.
2	98	—	1	—	1.26	193 — 197	3.6 at 218° C.
2	98	—	—	1	1.11	214 — 230	1.1 at 218° C.
5	95	1	—	—	1.33	209 — 217	4.1 at 219° C.
25	75	1.5	—	—	1.38	208 — 218	3.5 at 220° C.
95	5	0.5	—	—	1.41	170 — 176	4.1 at 219° C.
2	98	—	—	—	1.15	178 — 184	0.1 at 218° C.
25	75	—	—	—	1.20	178 — 184	0.9 at 218° C.
95	5	—	—	—		177 — 182	12.3 at 219° C.

The block graft polymers prepared according to this invention may for example be homogeneously mixed with polyformaldehyde:

(a) 20 parts of the block graft polymer derived from 5 parts of polyformaldehyde and

95 parts of polycaprylolactam are mixed with 80 parts of polyformaldehyde having the properties set out in Table 2, and this mixture is intensely kneaded for about 30 seconds in a twin-shaft disc type kneader at 190° C.

to 205°C. A homogeneous mixture having the density 1.40 g/cc, the melting range 178°C to 182°C and the melt index of 1.13 at 195°C is obtained which can be kept for twelve hours at 160°C without loss of weight or other noticeable damage.

(b) 30 parts of the block graft polymer derived from 25 parts of polyformaldehyde and 75 parts of polycaprylolactam are mixed with 70 parts of polyformaldehyde having the properties set out in Table 2, and this mixture is kneaded under the conditions specified under (a). In this case also, a homogeneous mixture is obtained which can be kept for 12 hours without loss in weight or other marked damage at 160°C. The mixture has the density 1.35 g/cc, the softening range 177° to 181°C and a melt index at 195°C of 0.435 and absorbs only 0.95% by weight of water on lying in boiling water for an hour. Polyformaldehyde having the properties set out in Table 2 on the other hand absorbs 1.8% by weight under these conditions and the polycaprylolactam used in this Example 25 4% by weight. The mixture may be processed

into mouldings, such as gears and casings, by injection moulding.

EXAMPLE 4.

A mixture consisting of (a) 15 parts of polyformaldehyde and (b) 55 parts of high-pressure polyethylene having the properties set out in Table 2, (c) 30 parts of polyamide having the softening range 222° to 226°C and the melt index 1.6 g/10 min., at 235°C., prepared in the usual way from 20 parts of caprylolactam and 80 parts of the salt of 4,4'-diaminodicyclohexylmethane and heptadecanedicarboxylic acid, and (d) 0.5 part of tertiarybutyl peroxide, is intensely kneaded for about 70 seconds in a twin-shaft disc type kneader and then granulated in the conventional way. An elastic thermoplastic block graft polymer is obtained which absorbs 0.70% by weight of water on lying in boiling water for one hour and which has the properties given in Table 4. Column A gives the property, column B gives the specification by which it is measured, column C gives the measured value and column D gives the units in which the measurement is made.

30 35 40 45 50

TABLE 4

A	B	C	D
Density	DIN 53,479	0.99	g/cc
Softening range		138 — 152	°C.
Dielectric constant at 10 ⁶ cycles	DIN 53,483	2.8	
Dissipation factor tan δ at 10 ⁶ cycles	DIN 53,483	0.001	
Melt index at 193° C.	ASTMD—1238—T	0.21	g/10 min.

The block graft polymer may be used with advantage for the production of packaging containers.

EXAMPLE 5.

55 A coarse mixture of 70 parts of polyformaldehyde having the properties given in Table 2 and 30 parts of a copolymer having the density 1.08 g/cc and the K-value 72 (measured according to H. Fikentscher, Cellulose-Chem. 13, page 58 (1932)) prepared in the conventional way from 74 parts of styrene and 26 parts of acrylonitrile, is intensely kneaded with 1 part of tertiarybutyl per-

oxide under the conditions given in Example 1.

65 A block graft polymer (a) is obtained which is suitable for example for the production of mouldings by injection moulding. The properties of the polymer (a) are compared in Table 5 with a mixture (b) which has been prepared from the same initial materials without adding the catalyst but otherwise in an identical way. Column A gives the property measured, column B gives the specification by which it is measured, column C gives the measured value and column D gives the unit by which the measurement is made.

65 70 75

TABLE 5

A	B	C	D
		a	b
Melt index at 190° C.	ASTMD 1238-T	5.74	9.16
Density	DIN 53,479	1.30	1.28
Melting range	172—179	135—170	°C.

EXAMPLE 6.

98 parts of polyformaldehyde prepared in conventional manner and having the density 5 1.423 g/cc., the softening range 183° to 185°C and the melt index 15.6 g/10 min. at 190°C is mixed with 0.1 part of dicumyl peroxide, 0.5 part of hexamethylene diisocyanate and 2 parts of polypyrrolidone prepared in conventional manner and having the K-value 86 10 and the melting point 272°C (with decomposition). The mixture is plasticised and homogenised in an extruder at a velocity gradient

of 19,800 sec⁻¹. A thermoplastic, homogeneous and stable graft polymer is obtained which has very good dimensional stability (elasticity modulus 37,300), a tensile strength of 800 kg/sq. cm and the density 1.40 g/cc. 15

The following Table 6 shows the loss of weight, due to depolymerisation, of the graft polymer when kept at 213°C under nitrogen as compared with the loss of weight of the initial materials subjected to the same conditions. 20

TABLE 6

Heating Period (minutes)	Weight Loss of		
	Polyformaldehyde	Polypyrrolidone	Graft Polymer
30	52%	15%	0.7%
60	78%	23%	1.9%
90	91%	28%	1.6%
120	97%	32%	1.8%

WHAT WE CLAIM IS:—

1. A process for the production of block graft polymers wherein a high molecular weight polyformaldehyde is intensely kneaded 30 (as hereinbefore specified) with one or more other thermoplastic synthetic resins with the addition of a small amount of a free radical forming organic catalyst. 45
2. A process as claimed in claim 1 wherein the polyformaldehyde has a melt index between 8 and 40 g/10 min at 190°C. 50
3. A process as claimed in claim 1 or 2 wherein said other thermoplastic synthetic resin has a melt index between 0.4 and 50 40 at a temperature 10°C above its melting point. 55
4. A process as claimed in any of claims 1 to 3 wherein the catalyst used is an organic peroxide, an azo-bis-nitrile or an azo disulphonate.
5. A process as claimed in any of claims 1 to 4 wherein the kneading takes place at a temperature between 100° and 210°C. 50
6. A process as claimed in any of claims 1 to 5 wherein the kneading takes place in a machine providing shear stresses between 100 and 1.5×10^3 kg/sq.cm. and velocity gradients G between about 10 and 2000 seconds⁻¹. 55
7. A process as claimed in any of claims 1 to 6 wherein the components are first pre-mixed in conventional mixing machines.
8. A process as claimed in any of claims 1 to 7 wherein additives which do not react with the catalyst under the conditions of kneading are added to the components.

9. The process of claim 1 carried out substantially as described in any of the foregoing Examples.

5 10. Block graft polymers when obtained by the process claimed in any of claims 1 to 9.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1965. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.